This work presents five years (two years of new data) of seasonal (winter v summer) data on dissolved N2O concentrations in the Elbe River Estuary. The insights this can provide into interannual variations in aquatic N2O is relatively unique. The site of the study itself, which encompasses a large industrial port, is also important in terms of better understanding anthropogenic impacts on aquatic N2O emissions. The authors show that, even though the source of N2O seems to be strongly seasonal, emissions remain relatively consistent over the year. This is a new and interesting finding. Overall this is a nice study with the potential to be a useful contribution to both the journal and scientific understanding of aquatic N2O.

However, there are a few weaknesses with the data analysis and discussion that need to be addressed to ensure that the emissions are accurately represented and the findings are clearly conveyed.

We thank the reviewer for their constructive and helpful review of our paper as well as for the many great ideas to improve our research.

Following, we reply to each issue individually, and explain the changes we will make to the revised manuscript to meet the reviewers criticism. Reviewer comments are written in bold italics, our answers are kept in plain font.

1. Converting dissolved concentrations to emissions: Like many studies, here the authors measured the dissolved concentration of the gas (N2O), and then converted this into water-air emissions based on a gas transfer velocity (k). Gas transfer velocities can be highly variable, especially in estuaries where the importance (and magnitude) of factors like wind, flow velocity, and water depth can all vary a lot over space and time. This complexity is reflected in the wide range of empirical k value parameterisations that have been developed for estuaries (see e.g., Rosentreter et al. (2021), also Hall and Ulseth (2019) for a good review of the topic, albeit for freshwater systems). However, here the authors convert measured concentrations to emissions using a single parameterisation (L116-125). This creates considerable uncertainty, which is not reflected in the reported estuary emissions estimates. Emissions should be recalculated using 3-5 k parameterisations, and the variability of these outputs reported in the results / figures. More information should also be supplied on the wind speed data used in the parameterisations. It is important to understand how the values measured during the campaigns compare to 'average' conditions around the estuary when considering the upscaled seasonal emissions values (e.g., are emissions estimates likely to be on the low side because cruises were only done on low-wind days?).

Thanks for this helpful comment. As suggested we will include calculations using two other parameterizations and report the variability. We will calculate and discuss the effect of wind speeds in relation to average conditions along the estuary as well as add the information about average wind speed. In general, long-term average wind speeds along the Elbe estuary range between 2.8 and 5.8 m s^{-1} (https://www.dwd.de/DE/leistungen/windkarten/deutschland_und_bundeslaender.html, last accessed: 05.04.2023).

2. Relationship between N2O and N inputs: As discussed in the paper intro here, aquatic N2O emissions are generally predicted based on N loads to the system (i.e., leaching of N, inputs from WWTPs, etc). While here N2O emissions are discussed and presented, the N inputs side of the equation is not clear to me. In the site description it says that annual N load were ~80 Gg y-1 (L67) – but does this mean the estuary receives this much N, or discharges this much N? And how does this break down between sources (WWTPs v river discharge)? On L231 it says that N2O emissions were low relative to other high N input estuaries. But how do N inputs into the Elbe stack up compare to these other estuaries? I particularly wonder how the 'point source' N loads around the port might stack up with those in other urban estuaries where N2O emissions have been measured, e.g., (Wells

et al., 2018). Constraining the other side of the N2O emissions v N inputs equations is critical for placing these findings into a more global context. Within the study, more information on N loads will also be important for picking apart the seasonal emissions drivers. How much N enters the estuary at the port? Is this input seasonally variable? Did it vary between the sampled years? Do these variations correspond with variations in emissions (particularly the size of the winter N2O-excess excursion)?

The N-loads of 80 Gg yr^{-1} are calculated from concentrations data at a station "Seemanshoeft", which is located at the Hamburg Port (stream kilometer 628.9). In general, point sources play a subordinate role in the nitrogen input of the Elbe estuary (Hofmann et al., 2005; IKSE, 2018) with dominating agricultural sources in the upper and middle Elbe River (Hofmann et al., 2005; Johannsen et al., 2008). We will add this information to the study site description. Further, we will calculate annual varying DIN and total nitrogen (TN) loads for our observation period and list the results in the supplements as recent TN loads were lower varying between 40.67 kt-N yr^{-1} and 60.08 kt-N yr^{-1} from 2015 to 2021 (FGG, 2021).

We will restructure our section 4.5 of the discussion: We will address the N_2O emissions and N inputs relation based on a comparison of the amount of DIN released as N_2O for annual loads and for each cruise separately. In a revised version, we will compare flux densities and the N_2O emission versus N input equation to a wider set of literature data and further estuaries. We will more clearly refer to a change of drivers for N_2O emissions in winter (high riverine input and nitrification) versus spring and summer (organic matter). Finally, we will highlight the link of N_2O emissions to eutrophication phenomena to broaden the scope of our paper.

1. Introduction: It is not entirely clear how studying N2O in the Elbe estuary will advance understanding of aquatic N2O emissions / fill a needed research gap. A stronger transition between the penultimate and last paragraphs of the discussion is needed (how does the present study relate to the broader literature). Stating a testable hypothesis, rather than just site-specific study objectives, in the last paragraph may also help make the study more clearly relevant to the broader scientific community. Is this just a case study or will the data help us understand estuary N cycling and gaseous emissions in a more fundamental way?

Thanks for this great comment! We will focus on the connection to a broader scientific audience, likely by stressing the general link of N_2O emissions and eutrophication phenomena in heavily managed estuaries around the world. So that overall, we provide a better insight of controls on seasonal varying N_2O production and emissions from heavily anthropogenic impacted estuaries.

2. Discussion: While I think overall the data interpretation makes sense, the discussion section currently reads as a bit descriptive and could go further to place these findings in a broader context (rather than just the context of how we understand the Elbe River Estuary). This could include in particular more discussion of N cycling in urban estuaries / where there are point N pollution. Where else in the world would the observed seasonal patterns be expected to be found? I also think there is missing some discussion of 'alternative hypotheses' – work through the logic of why denitrification is not thought to be the primary driver of N2O in the estuary, and why benthic production (e.g., (Chen et al., 2022)) is also ruled out. Also please carefully edit to ensure that you are not repeating results in this section.

We will discuss the alternative hypotheses in more detailed as we described below in the replies for the individual comments. We want to clarify that we found both denitrification in the sediments as well as production in the water column responsible processes for N_2O production in the Port of Hamburg. However, we will discuss the effects of benthic fluxes and production in more detail (see specific comment below). In a revision, we will carefully remove results bits from the discussion section, and will focus more on comparing our finding with research from other estuaries to address a broader audience.

3. Conclusion: This is currently very focused on untangling what exactly is happening within the Elbe River Estuary, but the implications for broader understanding of aquatic N2O production and emissions are not clear.

We will add a section about the implications for a broader understanding by (1) addressing our newly formulated hypothesizes as well as (2) summarize the findings in a revised discussion section that will compare our findings to other estuaries.

L17-19: This sentence is not clear (how does N2O 'compensate' for decreasing N loads?), please reword.

This statement was supposed to summarize our findings of section 4.1, where we complemented observations done by Brase et al. (2017) with our new data sets: Previous N_2O measurements done in 1980s and 1990s showed a significant reduction of N_2O saturation due to reduced riverine nitrogen loads and higher dissolved oxygen conditions. Water quality in the Elbe estuary improved significantly after the reunification and collapse of East German industries (e.g. Guhr et al., 2000). In the 1980s, high nitrogen loads and low oxygen conditions favored denitrification leading to high N_2O saturations (Hanke and Knauth, 1990). With improving water quality, the importance of denitrification decreased (Dähnke et al., 2008), which probably led to the decrease in N_2O saturations (Brase et al., 2017). However, compared to the study in 1997 (Barnes and Upstill-Goddard, 2011) our measured N_2O saturations did not further decreased despite a continuous reduction of nitrogen loads entering the estuary form the upstream river (e.g. Figure 5, FGG Elbe, 2018; Radach and Pätsch, 2007). These findings suggesting that in-situ N_2O production along the estuary is important and compensates the overall effect of decreasing nitrogen loads in the last decades.

Also considering previous reviewer comments we will address the importance of our research for a broader audience in the abstract and thus, rephrase or remove this finding from the abstract. Instead, we will probably address the results from the comparison of our results with other research and the implications for other heavily managed estuaries (see comment above).

L22-24: "In winter, high riverine N2O concentrations led to high N2O emissions from the estuary, whereas in summer, estuarine biological N2O production led to equally high N2O emissions." This is I think getting at a crucial point (that although seasonal magnitude of N2O fluxes did not differ the drivers of these fluxes did), the meaning is not clear. What is the difference between winter 'high N2O concentrations' and summer 'high N2O production'? Reword to be more precise about these differences.

We wanted to address the seasonal varying drivers leading to high N_2O emissions along the Elbe estuary. We will rephrase the section of the abstract.

L70: How often is 'on a regular basis'? e.g., weekly, yearly, every three years?

Deepening and dredging operations in the Elbe estuary are performed year-round, if necessary every couple of days. We will clarify this.

L86: Suggest changing 'steaming upstream' to 'travelling upstream' (steaming sounds a bit antiquated)

We will change the wording as suggested by the reviewer.

L101-104: More information on number of nutrient samples collected per survey, as well as method detection limits and precision, would be useful.

We usually took about 30 to 40 samples during each cruise. We will include the detection limits and also add a short description addressing the range of samples numbers.

L109: How often was 'regularly'? e.g., before each cruise?

We measured standard gas mixtures before and after each day of our campaigns that usually lasted from two to three days. We will clarify this in a revision.

L116: How often, and how, was dry air sampled during each cruise?

We measured dry air before and after each day, as with standard gas mixtures. Also, we continuously measured dry air overnight in between our sampling days. We will include this in the text. We used an air duct from the deck of our research vessel into our analyzer.

L122: The term 'flux densities' is not one I'm familiar with – more common to see something like 'water-air fluxes' or 'evasion'.

We used the term "flux densities", because we had both positives and negative fluxes. Therefore, we would like to stick to this term, which has been used previously (e.g. Brase et al., 2017; Bange et al., 2019; Morgan et al., 2019; Forster et al., 2009). However, we will insert a brief definition of the term.

L123-125: Please provide some clarification on the upscaling approach used to calculate whole-estuary emissions. From the description it sounds like the mean flux was multiplied by the estuary surface area? Or were these calculations area-weighted, and if so at what resolution?

We multiplied the mean flux with the estuary surface area. Due to the comment of the other reviewer, we decided to change our calculation approach and to calculate mean fluxes for three different regions: 1. Limnic and Hamburg Port region, 2. Oligohaline section and 3. Mesohaline/Polyhaline section while separating our data set into seasons (winter: March, spring: April and May, summer: June and July, late summer: August and September). We will use this data to calculate annual emissions from the entire estuary. Further, we will calculate flux densities and emissions for various wind speeds (wind during our cruises, annual and seasonal average wind speeds). We will clarify this method in the reviewed version of our manuscript.

L127-128: Citation?

We will add a citation (e.g. Nevison et al., 2004; Walter et al., 2004).

L148: Low relative to what?

"low" is less than 1 µmol L^{-1} – we will specify this.

L163-189: Separating the N2O data into different sections for the different units (molar concentrations, % saturation, water-air fluxes) is confusing as these are all inter-related. For instances, it is hard to make sense of the meaning of the molar concentrations without also considering whether these reflect changes in percent saturation (i.e., changes due to water temperature / salinity v source / production). I suggest integrating these lines of data (and thinking) to provide a clearer picture of estuary N2O patterns.

We will change N_2O concentrations to N_2O saturations in Fig. 2. Thus, we will remove Fig. 3 in the text. As suggested by the reviewer in a comment below, we will focus on describing N_2O saturations rather than concentrations to exclude effects on N_2O solubility.

L204: High relative to what?

"High" is more than 100 % – we will specify this.

L209-218: The AOU v N2O-excess relationship really highlights the importance, and seasonality, of the port for estuary N2O emissions, with distinct peaks in the winter and consumption in the summer. Given that this underpins the discussion around seasonal N2O source switching, I wonder if there is a way to include more than just these 'representative' plots in the main text. For instance, a table with info on AOU v N2O-excess slopes, and min-max range for the port? I think if the port data is excluded something like an ANCOVA could be used to compare shifts in slope relationships.

In the Port region, N_2O_{xs} and AOU had no linear relation during most of our cruises (e.g. June 2015 and August 2017). Therefore, a table with slopes and min-max ranges would miss crucial information. However, we will include figure S2 from the supplement in the main text so that we do not only show representative plots but all cruises. We will further test whether an individual (i.e., over distinct sections) assessment of slopes aids the discussion.

L256-260: Interesting relationship between NO2- and N2O. This could be connected to previous work, e.g., (Sharma et al., 2022; Smith and Bohlke, 2019; Wertz et al., 2018)

Thanks for these suggestion. We will address previous works that found a relation between N_2O and nitrite in a revised version of our manuscript. In our data set, the accumulation of nitrite is a sign for stepwise nitrification rather than denitrification, which is in contrast to findings from e.g. Wertz et al. (2018) and Sharma et al. (2022).

L314-316: This should be in the results section

We will add a section about the statistical analysis in the results section and will move this bit into this new section.

L318-324: Interesting! I wonder if the algae themselves could also be contributing to the N2O production, e.g., (Fabisik et al., 2023)

Thanks for this great literature suggestion. We will address their findings briefly in a revised version of our manuscript.

L330-332: This makes sense, but is this the only possible explanation for high emissions around the port area? What about wastewater inputs, enhanced benthic production, and/or enhanced groundwater connectivity due to dredging? Some discussion of these points will make this conclusion stronger.

Thanks to the reviewer for this helpful comment. We largely ruled out most of these sources, but will certainly discuss this in more detail in our revised version. First, point sources (including the waste water treatment plant, WWTP) are considered to be from only minor importance in the Elbe estuary (Hofmann et al., 2005; IKSE, 2018). Further, we estimated the impact of the WWTP as less than 5 % even under low fresh water inflow. We will address this in the study site description.

We found no general trend between turbidity values and N_2O saturation. Thus, we excluded an overarching effect of deeping and dredging operations on N_2O levels, which we discussed later in the text (L:349 – 352).

We considered both sediment denitrification and water column nitrification responsible for the elevated N_2O saturations. We will discuss the different explanations for high emissions in the port and partly restructure the discussion in section 4.3 in line with the suggestion of the reviewer.

L357-358: How extreme was this rain event, i.e., was it more extreme than any rainfalls over the other five years of sampling? This will help verify the attribution, and also put the pulse into context. It would then be instructive to recalculate the seasonal budget with and without this pulse.

The rain event had a statistical recurrence probability of one to five years (https://sri.hamburgwasser.de/, last access: 04.04.2023). We will check the effect of this rain event on the seasonal budget. We will probably only present the data in the supplements, but we will address the resulting differences in the main text. Considering the statistical recurrence probability, it is likely that similar events occurred during the last five years, but so far not during a comparable sampling cruise. Moreover, we assume that temperature was equally important as water mass, because cold rain water in the waste water treatment plant led to aggravated operation conditions. Thus, in warmer months the effect might be different. We will discuss this in more detail in a revised version of our manuscript.

L392: If large riverine loads were the main driver, wouldn't there be a continuous decrease in concentration over distance? But instead emissions peak in the port.

N_2O concentrations were affected by a combined effect of river nitrate loads, and of additional production in the port region (L337-341). However, this production is also driven by river nitrogen loads, so that overall, river nitrogen or nitrate loads are crucial drivers of eutrophication as well as of N_2O production in winter. We will clarify this in this section of the text.

Table 2: Standard deviations for the air N2O concentrations would be helpful

We will include standard deviations.

Fig. 1: The most important pieces of info in this map (where sampling points are, where the port is, where the MTZ is) don't really stand out. Can you adjust colours, font size, etc to better highlight these key features? A scale bar for the main map would also be helpful.

We will change the style of map to highlight key features and important locations as suggested by the reviewer.

Fig. 2: I'm not sure that there is much value in showing N2O concentrations (in nM) here – the % saturation information in the subsequent figure is much more effective for showing fluctuations between seasons and over the salinity gradient, given the relatively low concentrations and the impact of both temperature and salinity on N2O solubility. It would also be helpful to have 'summer' and 'winter' headings at the top of the two columns to make the point of difference more immediately obvious.

We will include a heading to the plot and change N_2O concentrations to N_2O saturations. Thus, we will remove Fig. 3 from the text. We will move the plot and description of N_2O concentrations to the supplements.

Fig. 3: A unified y axis scale would be helpful for picking out seasonal differences

We decided against unified y-axis. Truly, it would help to visualize seasonal differences, but it would be hard to differentiate between the different cruises in spring and summer.

Fig. 4: As above, unified axes scales would make differences between sampling dates much clearer.

We decided against unified y-axis. The March 2021 cruise differs so much that it's hard to see variabilities in the other cruises if we use the same y-axis. However, we will use unified axes scales for all other cruises

Fig. 5: Different y axes are needed for the different variables (N2O, O2, TN), if not different plot panels

We will change the plot to include different plot panels for each variable.

Fig. 6: I found this to be too many variables on the same plot to make much logical sense out of. I suggest separating into two panels, one for all of the N species (y axis unit is uM N), and then another with two y axes, one for PN and one for C/N.

We will adapt the plot as suggested by the reviewer.

Fig. 7: It would be helpful to use a different pattern or colour scheme to distinguish the winter v summer cruises.

As we are planning to restructure this part of the discussion Figure 7 will most likely change. We will probably insert anew figure showing seasonal varying N_2O saturation, emission estimates, DIN loads and N_2O/DIN ratios to highlight the seasonal varying dynamic of these parameters and that N_2O emissions did not scale with DIN loads. Referring to a comment from the other reviewer, we will adapt this plot by separating the data into seasons (winter: March), spring (April and May), summer (June and July) and late summer (August and September). We will change the color scheme to better distinguish the winter season.

References

Bange, H. W., Sim, C. H., Bastian, D., Kallert, J., Kock, A., Mujahid, A., and Müller, M.: Nitrous oxide (N_2O) and methane (CH_4) in rivers and estuaries of northwestern Borneo, Biogeosciences, 16, 4321–4335, https://doi.org/10.5194/bg-16-4321-2019, 2019.

Brase, L., Bange, H. W., Lendt, R., Sanders, T., and Dähnke, K.: High Resolution Measurements of Nitrous Oxide (N2O) in the Elbe Estuary, Front. Mar. Sci., 4, 162, https://doi.org/10.3389/fmars.2017.00162, 2017.

FGG, F. E.: FIS der FGG Elbe - Physikalisch-chemische Qualitätskomponenten: Elbe - Bunthaus (Strom-km 609,8) - Wassertemperatur - Tagesmittelwert, 2021.

Forster, G., Upstill-Goddard, R., Gist, N., Robinson, C., Uher, G., and Woodward, E.: Nitrous oxide and methane in the Atlantic Ocean between 50°N and 52°S: Latitudinal distribution and sea-to-air flux, Deep Sea Res. Part II Top. Stud. Oceanogr., 964–976, https://doi.org/10.1016/j.dsr2.2008.12.002, 2009.

Hofmann, J., Behrendt, H., Gilbert, A., Janssen, R., Kannen, A., Kappenberg, J., Lenhart, H., Lise, W., Nunneri, C., and Windhorst, W.: Catchment–coastal zone interaction based upon scenario and model analysis: Elbe and the German Bight case study, Reg. Environ. Change, 5, 54–81, https://doi.org/10.1007/s10113-004-0082-y, 2005.

IKSE, I. K. zur S. der E.: Strategie zur Minderung der Nährstoffeinträge in Gewässer in der internationalen Flussgebietsgemeinschaft Elbe, Internationale Kommission zur Schutz der Elbe, Magdeburg, 2018.

Johannsen, A., Dähnke, K., and Emeis, K.: Isotopic composition of nitrate in five German rivers discharging into the North Sea, Org. Geochem., 39, 1678–1689, https://doi.org/10.1016/j.orggeochem.2008.03.004, 2008.

Morgan, E. J., Lavric, J. V., Arévalo-Martínez, D. L., Bange, H. W., Steinhoff, T., Seifert, T., and Heimann, M.: Air–sea fluxes of greenhouse gases and oxygen in the northern Benguela Current region during upwelling events, Biogeosciences, 16, 4065–4084, https://doi.org/10.5194/bg-16-4065-2019, 2019.

Nevison, C., Lueker, T., and Weiss, R. F.: Quantifying the nitrous oxide source from coastal upwelling, https://doi.org/10.1029/2003GB002110, 2004.

Sharma, N., Flynn, E. D., Catalano, J. G., and Giammar, D. E.: Copper availability governs nitrous oxide accumulation in wetland soils and stream sediments, Geochim. Cosmochim. Acta, 327, 96–115, https://doi.org/10.1016/j.gca.2022.04.019, 2022.

Walter, S., Bange, H. W., and Wallace, D. W. R.: Nitrous oxide in the surface layer of the tropical North Atlantic Ocean along a west to east transect, Geophys. Res. Lett., 31, L23S07, https://doi.org/10.1029/2004GL019937, 2004.

Wertz, S., Goyer, C., Burton, D. L., Zebarth, B. J., and Chantigny, M. H.: Processes contributing to nitrite accumulation and concomitant N2O emissions in frozen soils, Soil Biol. Biochem., 126, 31–39, https://doi.org/10.1016/j.soilbio.2018.08.001, 2018.